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National Renewable Energy Laboratory

Innovation for Our Energy Future

# Corrosion Protection of Metallic Bipolar Plates for Fuel Cells

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Project ID #: FCP12

# Overview

## Timeline

- Project start date: 2004
- Project end date: tbd
- Percent complete: tbd

## Budget

- Total project funding
  - DOE share: $196k
- Funding received in FY04: $40k
- Funding for FY05: $156k

## Barriers

- Barriers addressed
  - ✓ **Stack Material and Manufacturing costs.**
  - ✓ **Materials Durability**

## Partners

- Interactions/ collaborations
  - Oak Ridge National Lab.
  - Plug Power

# Approach and Objectives

- Our approach is two fold
  - Understanding the relationship between alloy composition and bipolar plate performance.
  - Study possible coating materials and methods.
- Objectives - FY 05 Goals
  - Corrosion testing of new alloys and coatings
  - Collaborate with ORNL to evaluate nitrided alloys and to determine best alloy composition for PEMFC.
  - Characterize conducting coatings on alloys and their performance in PEMFC environments.
  - Assemble test system for operation in the 100-200 °C range and study materials in this temperature range.
  - Development of corrosion tests for polyphosphoric acid environment at >150C

# Why Metallic Bipolar Plates

- Wide choices, high chemical stability, including choices for corrosion resistance
- High strength allowing thinner plates for high power density
- Existing low cost/high volume manufacturing techniques (e.g. stamping);
- High bulk electrical and thermal conductivities;
- Potential for low cost.

- DOE 2010 Technical Targets for Fuel Cell Stacks
  - -Cost $35/kW
  - -Durability 5000 hours

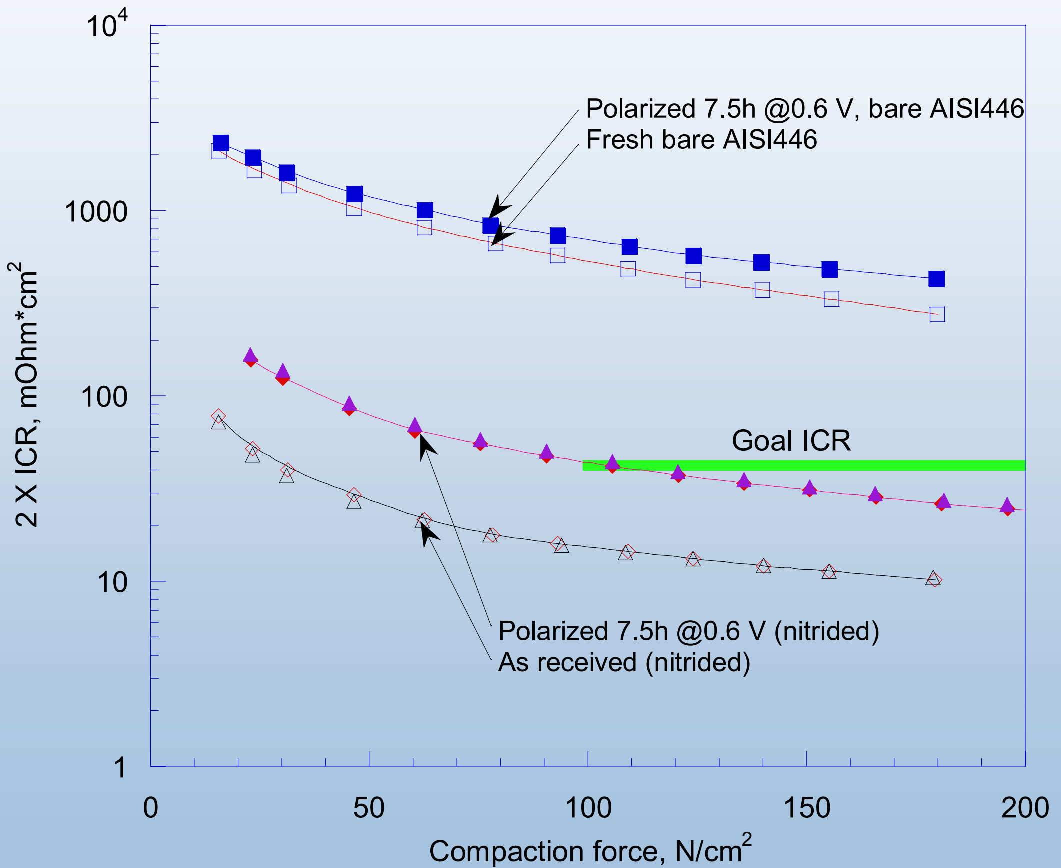
# Challenges with Metallic Bipolar Plates in PEMFC

- Possible contamination of polymer membrane by dissolved metal ions
- Higher surface contact resistance due to surface oxides (such oxides provide excellent corrosion resistance however)

# NREL/ORNL Collaboration

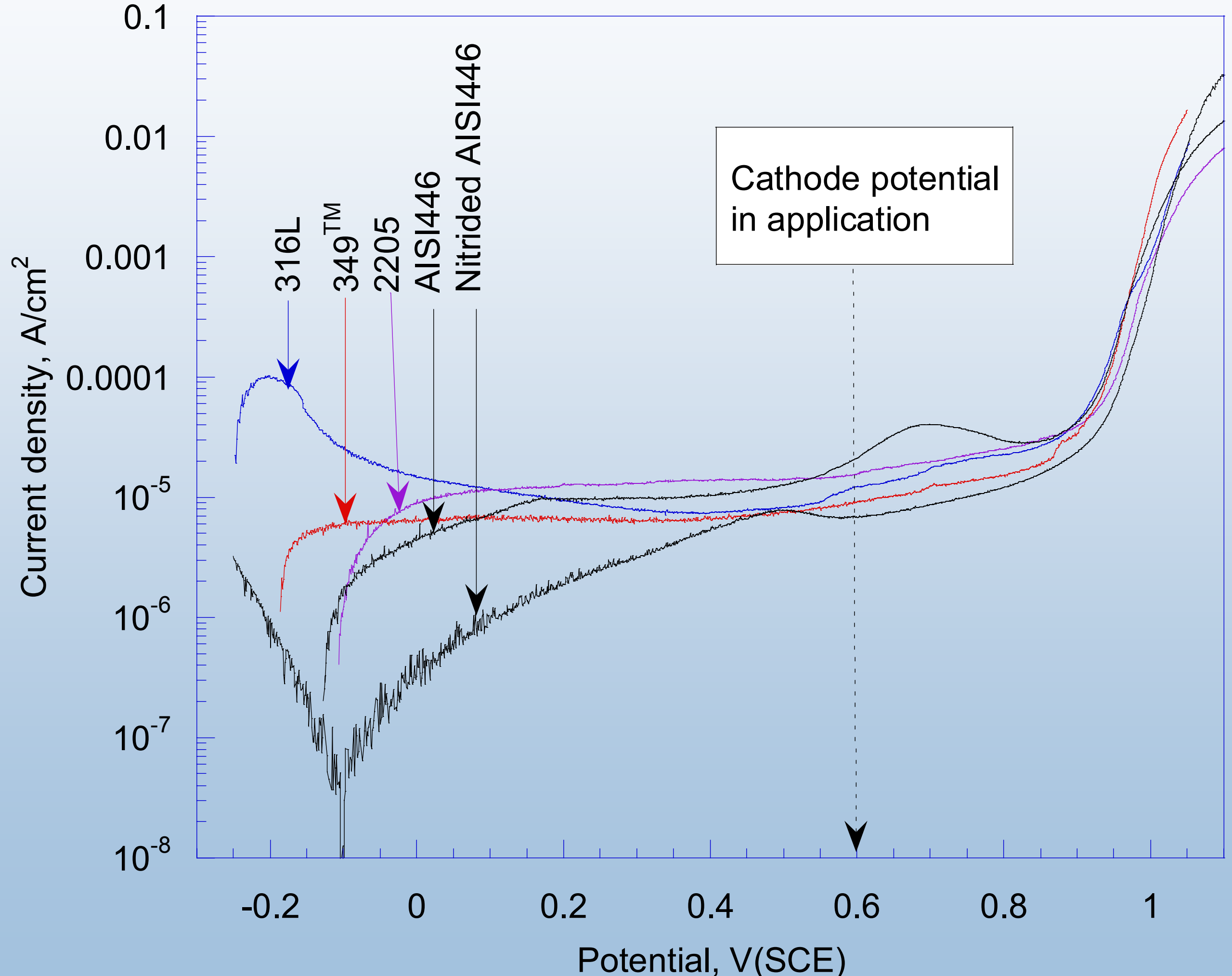
- Evaluated over 10 alloy compositions, both commercially available and synthesized;
- Evaluated the influence of nitridation parameters on the contact resistance and corrosion resistance in PEMFC environments, used for improving and adjusting the alloy composition and nitridation parameters;
- Filled a joint patent application for the nitridation of AISI446 alloy, finding 2 alloys suitable for PEMFC bipolar plates after nitridation.

# Initial Success for Fe-Cr alloy via Nitrogen Modified Oxide Layer

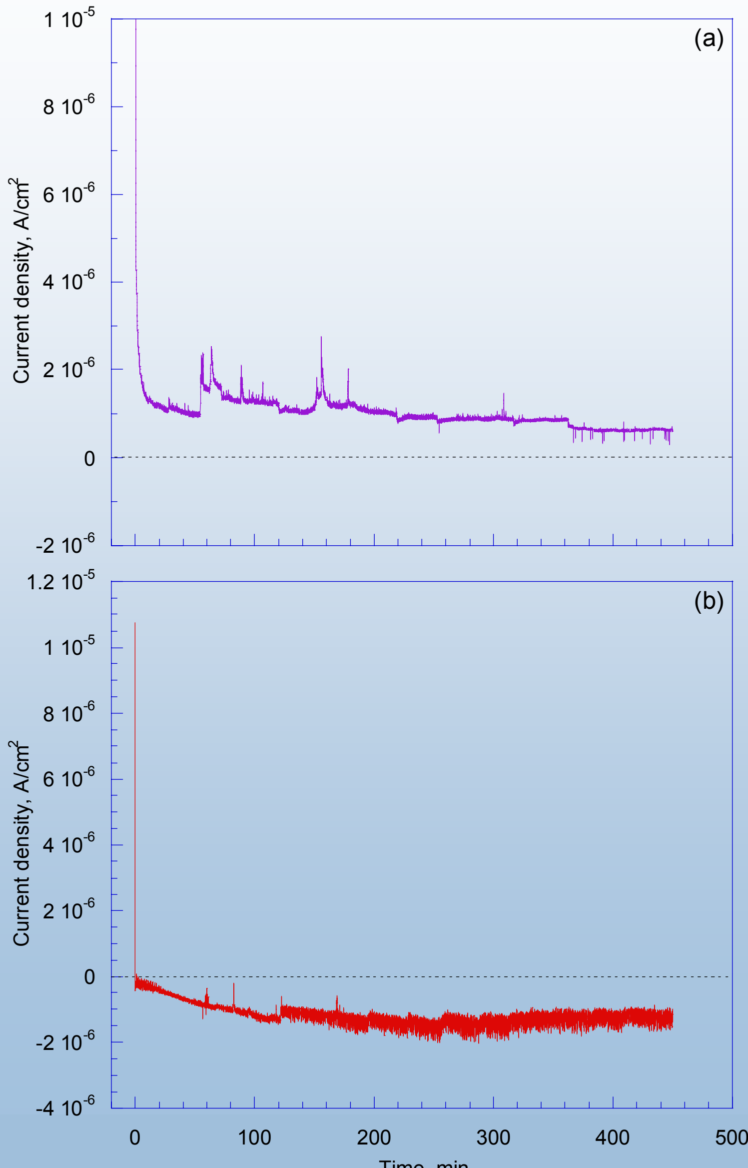



- AISI446 and Modified AISI446: Ferritic, Fe-base;
- ICR significantly decreased, both as-nitrided and tested;
- Surface complex of oxygen-nitrogen mixture with Cr, Fe.

# Nitrided AISI446 has excellent corrosion resistance in 1M $H_2SO_4$+2ppm $F^-$ at 70 °C with air purge

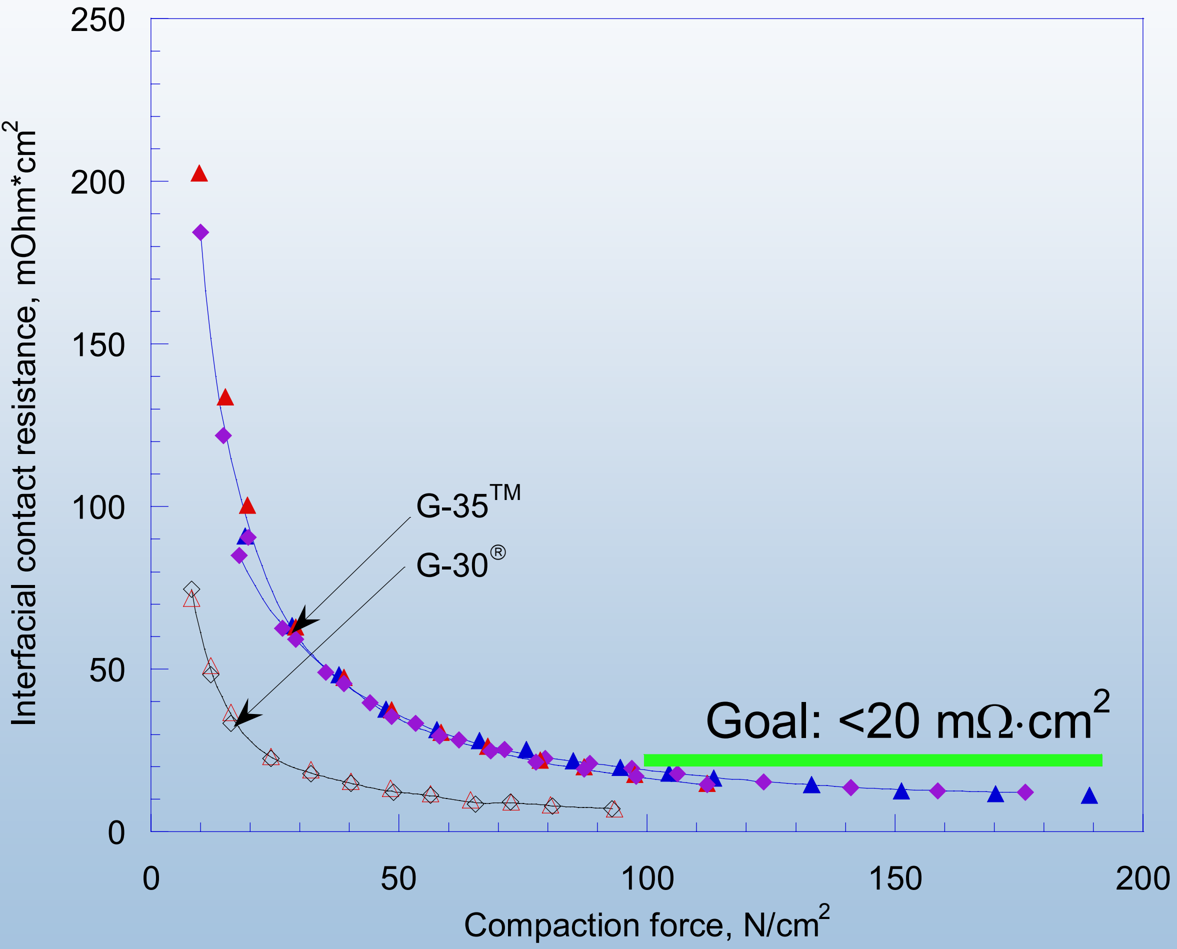


# Time-dependent data for Nitrided AISI446 in simulated PEMFC environments



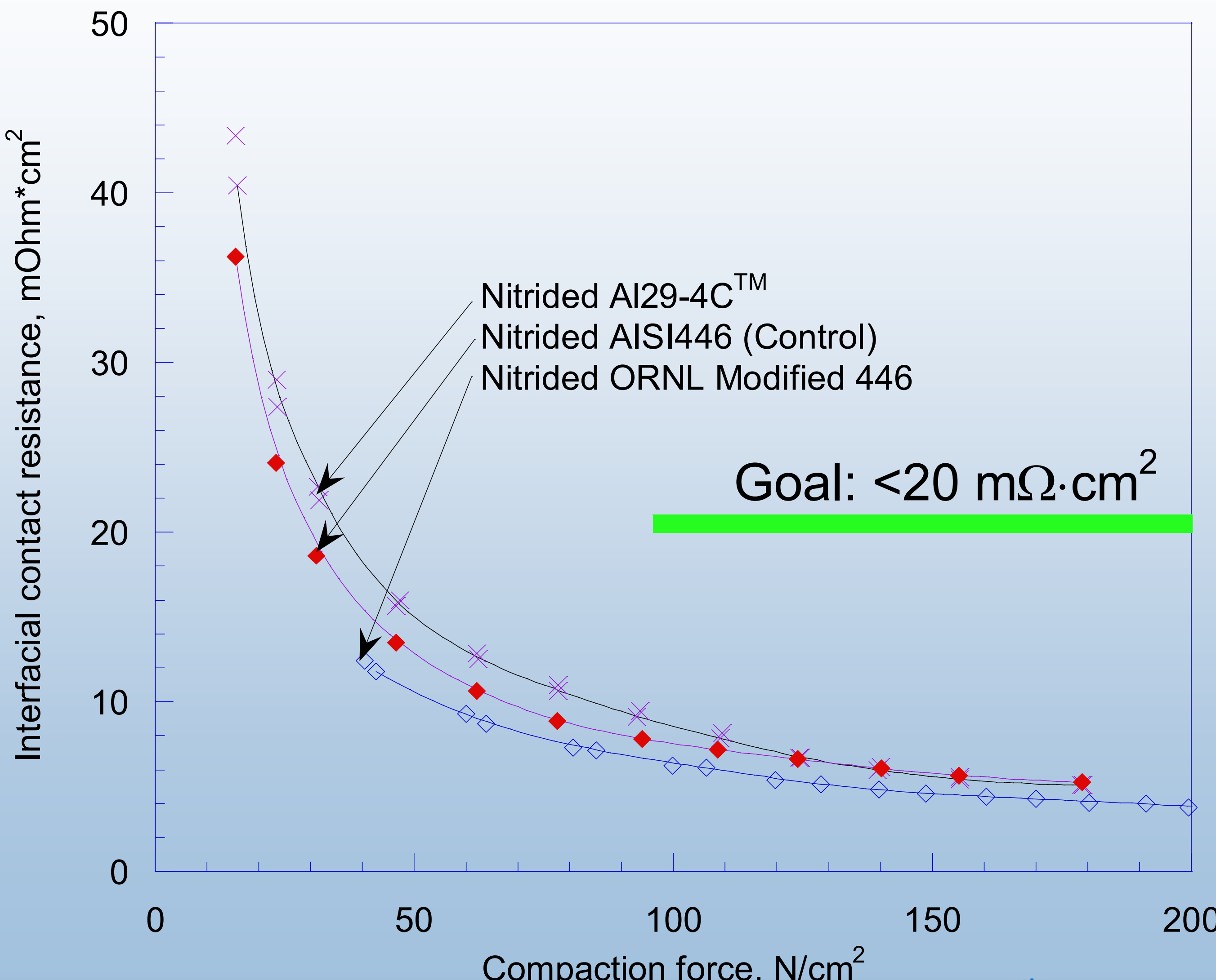

- Anodic behavior for nitrided AISI446 in PEMFC environments
  - cathode (a)
  - anode (b) (note the cathodic current).
- DOE target: 16 μA/cm$^2$

# Nitrided G-35™ and G-30® meet the ICR Goal

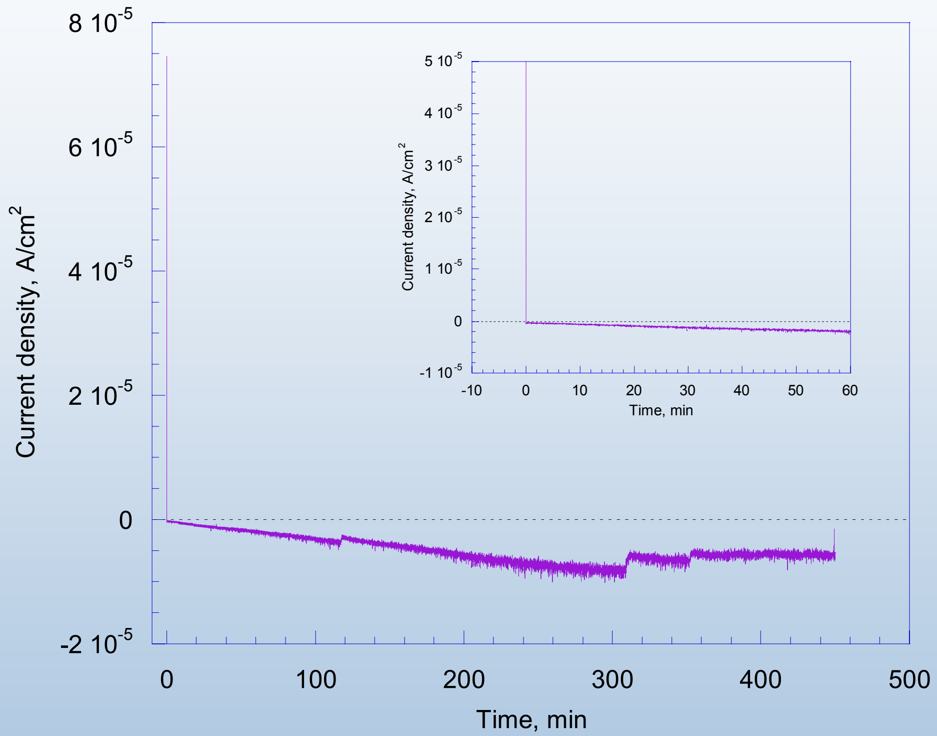



- Cr-nitrides formed on commercial Ni-base alloys;
- Corrosion test at GM and NREL show no increase in ICR;
- Complex conductive “oxy-nitride” after polarization (master’s thesis).

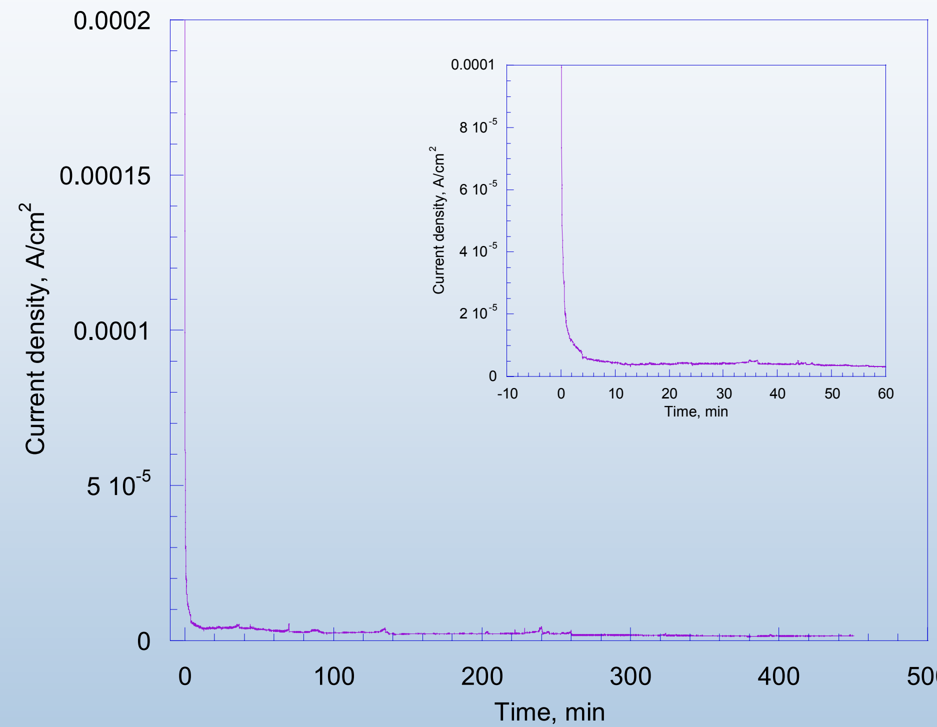
# Developing lower cost alloys with low ICR



# And keep excellent corrosion resistance after modification

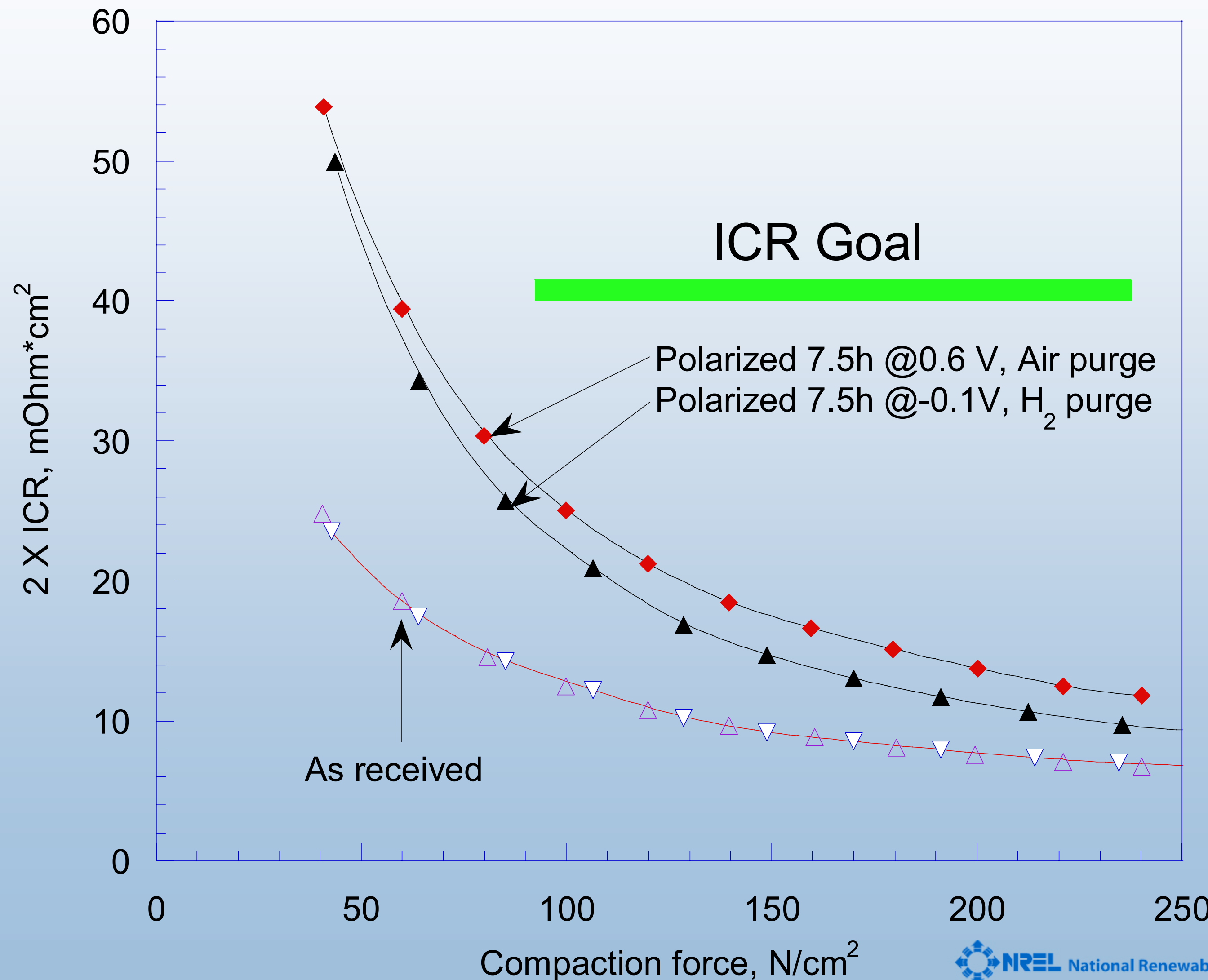



PEMFC anode




PEMFC cathode

# ICR for the modified 446 after polarization in PEMFC environments?



# Cost - DOE Targets

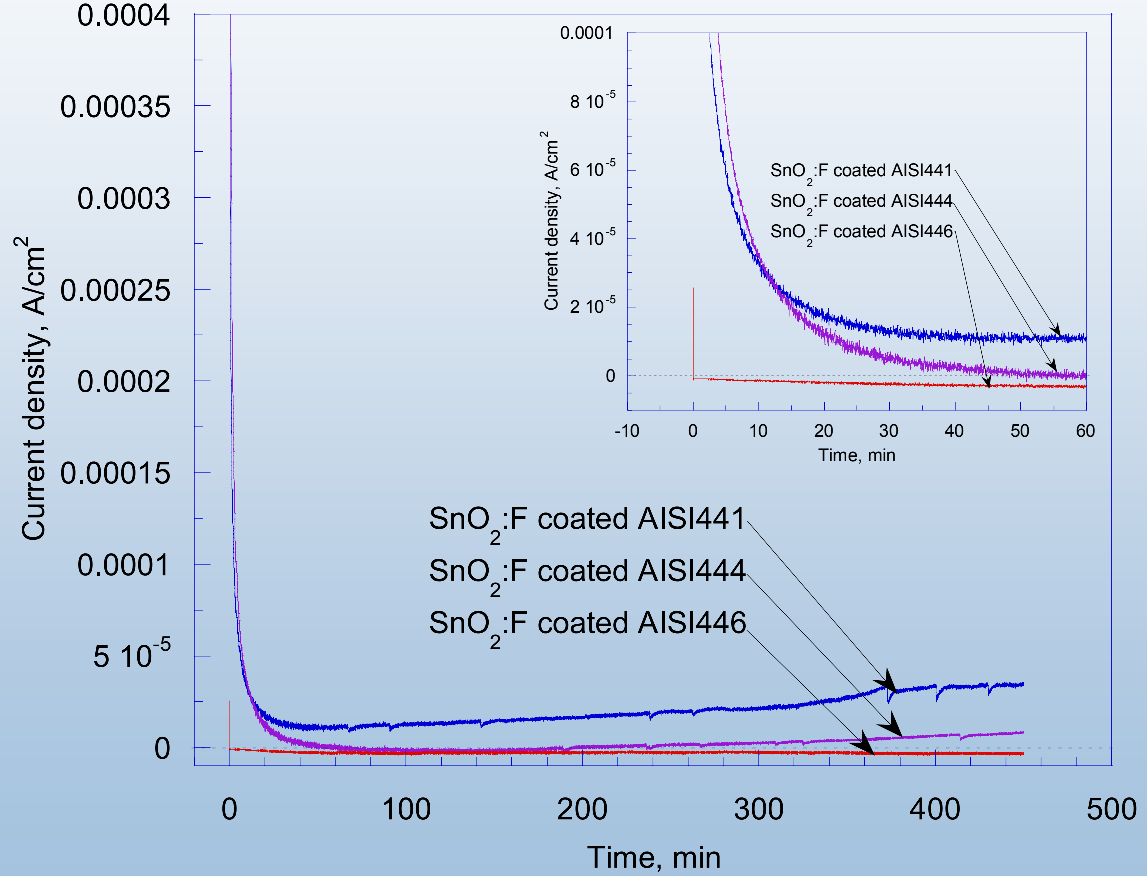
| Alloy | ICR@140 N/cm$^2$, m$\Omega$·cm$^2$ | Current at –0.1 V ($H_2$ purge), μA/cm$^2$ | Current at 0.6 V (air purge), μA/cm$^2$ | Cost*, $/kW |
|---|---|---|---|---|
| 349™ | 110 | -4.5~-2.0 | 0.5~0.8 | 4.22 |
| AISI446 | 190 | -2.0~-1.0 | 0.3~1.0 | 4.76 |
| 2205 | 130 | -0.5~+0.5 | 0.3~1.2 | 3.14 |
| **Nitrided AISI446** | **6.0** | **-1.7~-0.2** | **0.7~1.5** | **N/A** |
| **Modified AISI446** | **4.8** | **-9.0~-0.2** | **1.5~4.5** | **N/A** |
| ***DOE Target*** | ***20 m$\Omega$·cm$^2$*** | ***<16 μA/cm$^2$*** | ***<16 μA/cm$^2$*** | ***$10/kW*** |

Note: Cost data were based on the base price of cold rolled coils from Allegheny Ludlum (see website), and by assuming 6 cells/kW for a PEMFC and the dimensions of a bipolar plate are 24 cm × 24 cm × 0.254 cm (which gives a 400 cm$^2$ utilization surface area in a 0.01 inch thick sheet).

# Conductive $SnO_2$:F Coating

- High conductivity
- High stability in many different environments
- Volume production is available----widely used in PV industry
- May allow reduced cost with lower grade alloys.
- NREL expertise (National Center for Photovoltaics)

# Performance of coated steels in PEMFC anode environment




- Excellent behavior of $SnO_2$:F/AISI446 is expected;
- Good corrosion resistance of $SnO_2$:F/AISI444 is surprising! But match with ICP analysis (see Table)

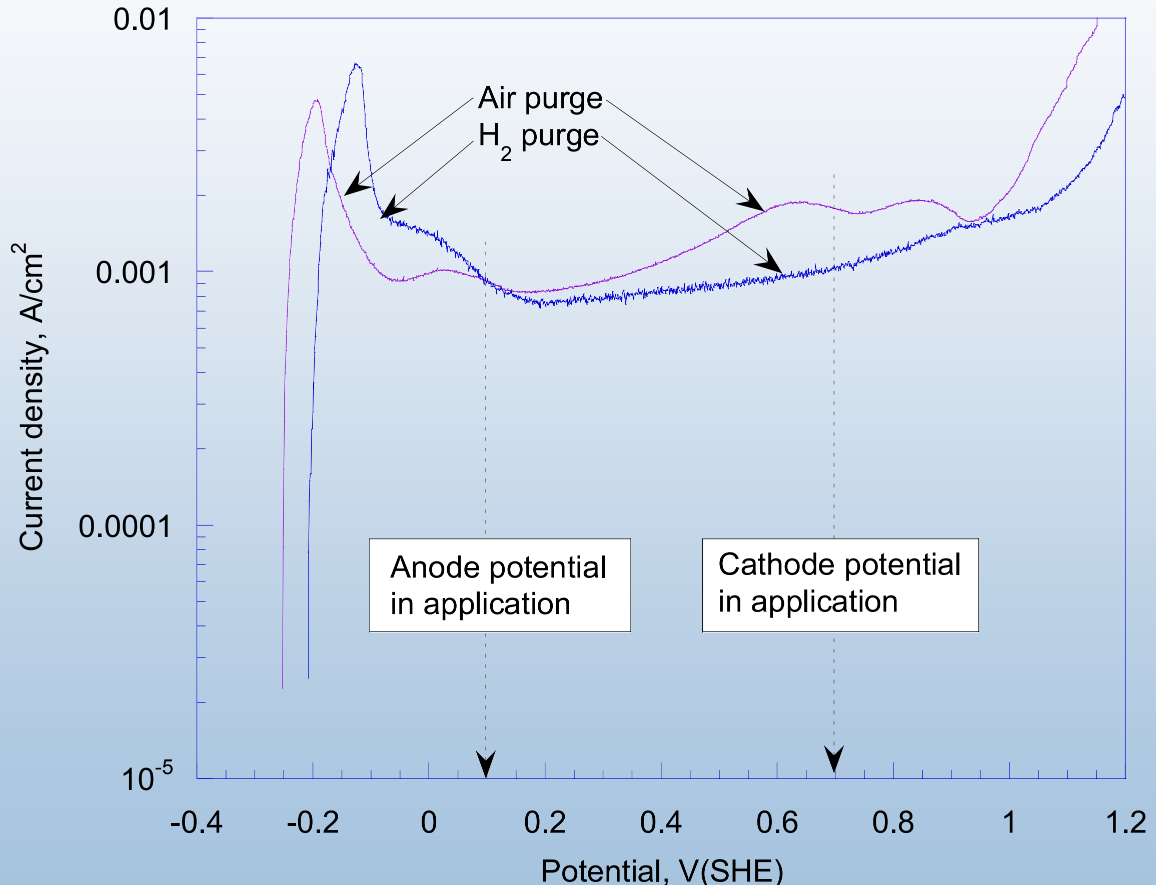
# Fe, Cr, Ni ions concentration after polarized in PEMFC environments (average of 3 samples)

| Material | Ion concentration in PEMFC anode environment after 7.5h | | | Ion concentration in PEMFC cathode environment after 7.5h | | |
|---|---|---|---|---|---|---|
| | Fe, ppm | Cr, ppm | Ni, ppm | Fe, ppm | Cr, ppm | Ni, ppm |
| 316L | 21.18 | 4.60 | 2.49 | 9.02 | 1.94 | 1.41 |
| 317L | 3.98 | 0.65 | 0.39 | 1.29 | - | - |
| 349™ | 1.70 | 0.12 | - | 1.47 | | |
| $SnO_2$/316L | 10.83 | 1.97 | 1.38 | 1.12 | 0.10 | 0.11 |
| $SnO_2$/317L | 4.03 | 0.69 | 0.56 | 0.87 | - | - |
| $SnO_2$/349™ | 1.27 | - | - | 1.07 | - | - |
| | | | | | | |
| 441 | 622.9 | 135.7 | 1.07 | 462.8 | 101.2 | 0.95 |
| 444 | 141.5 | 37.86 | 0.30 | 328.3 | 67.97 | 0.94 |
| 446 | 1.46 | - | - | 0.99 | - | - |
| $SnO_2$/441 | 24.15 | 4.51 | - | 330.3 | 68.72 | 0.60 |
| $SnO_2$/444 | 12.70 | 2.09 | - | 64.42 | 13.73 | 0.22 |
| $SnO_2$/446 | 1.24 | | | 0.98 | - | - |

# The Needs and Challenges of High Temperature (HT) bipolar plates ….Starting Point

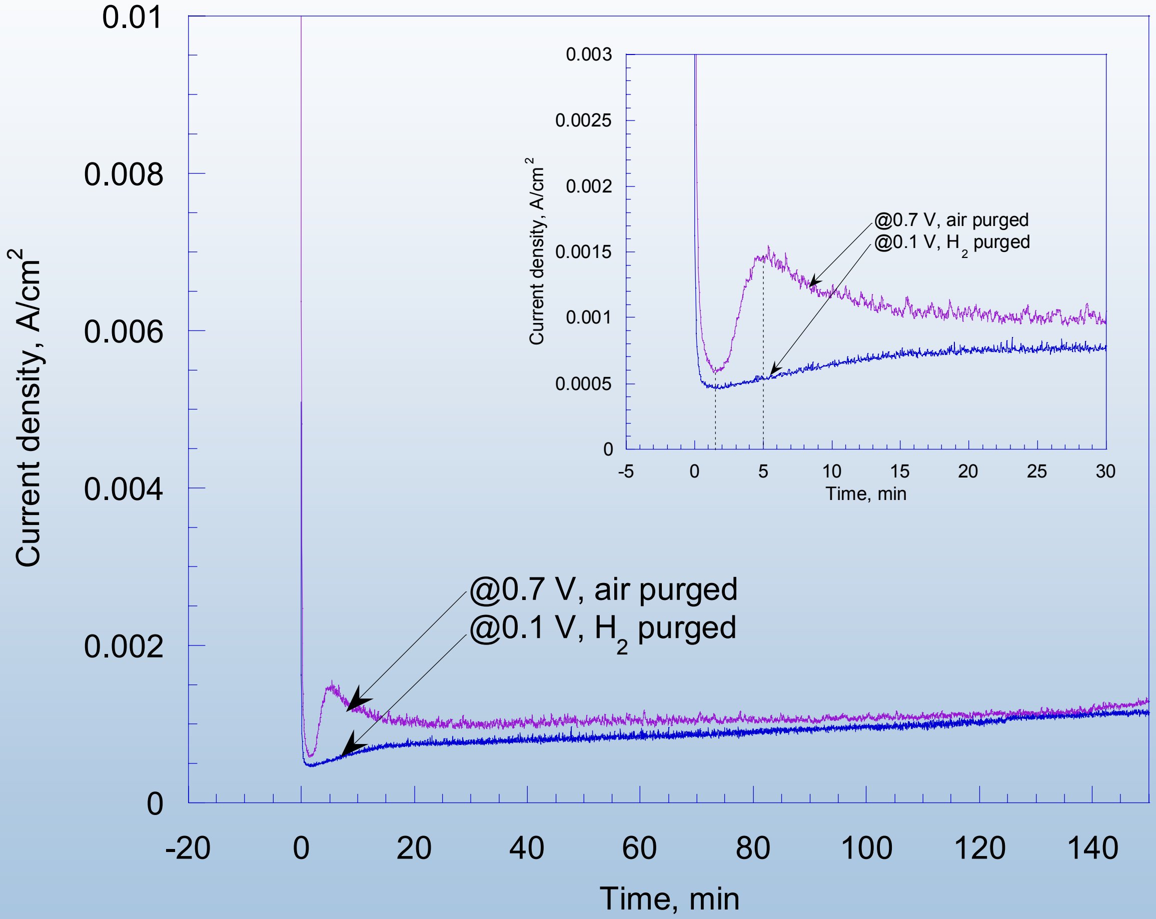
- Desire of transportation industry;
- R&D on high temperature membrane, however, <u>exact environments for HT PEMFC not yet defined!</u>
- Accordingly, set HT at 150 - 170 °C, selected $H_3PO_4$ as electrolyte, evaluated over 12 “HT” epoxies, and chose the best;
- Modified test systems to suite the HT, working with native stainless steel and graphite bipolar plate for PAFC from PlugPower.

# Dynamic polarization for 904L steel in $H_3PO_4$ at 170 °C



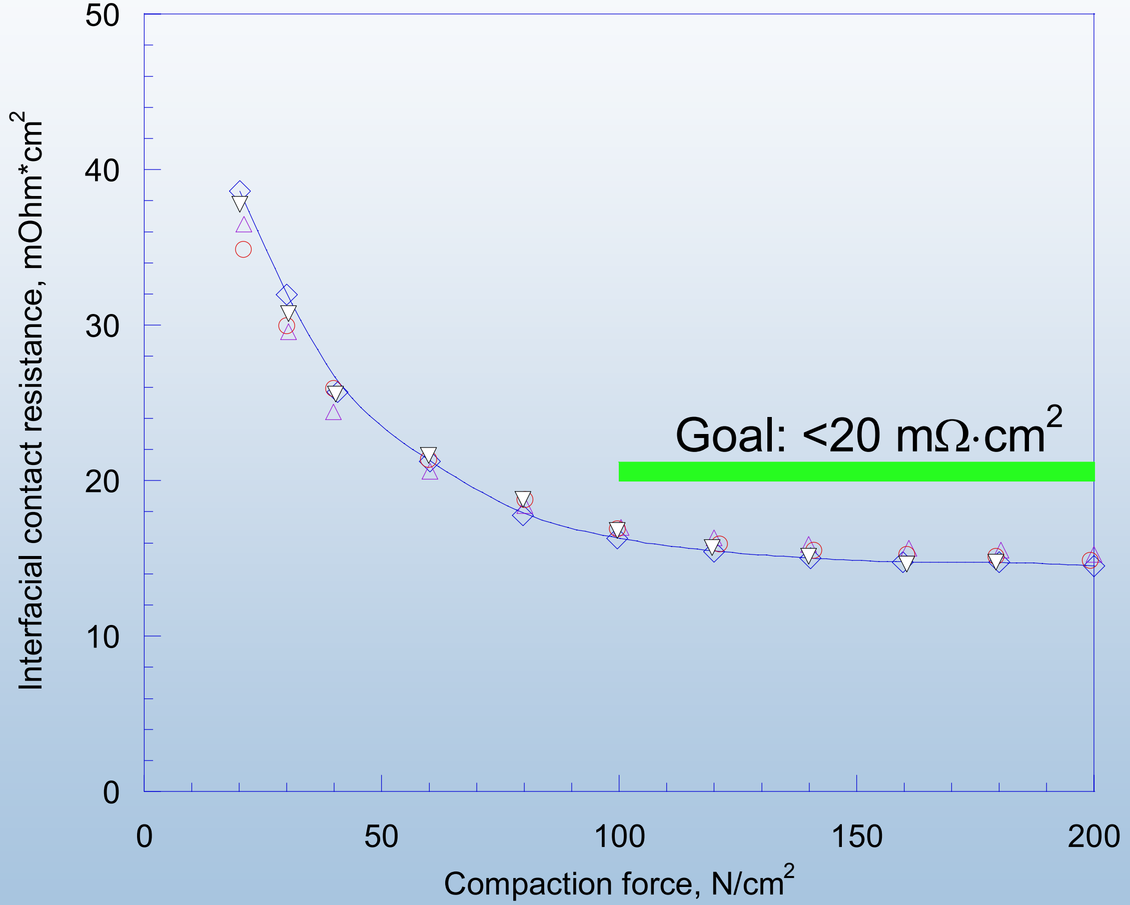

- New condition resulted in significant changes
- Passivation for the steel in both environments;
- High current noted even in the passivation region.

# How about potentiostatic polarization for 904L steel in $H_3PO_4$ at 170 °C?



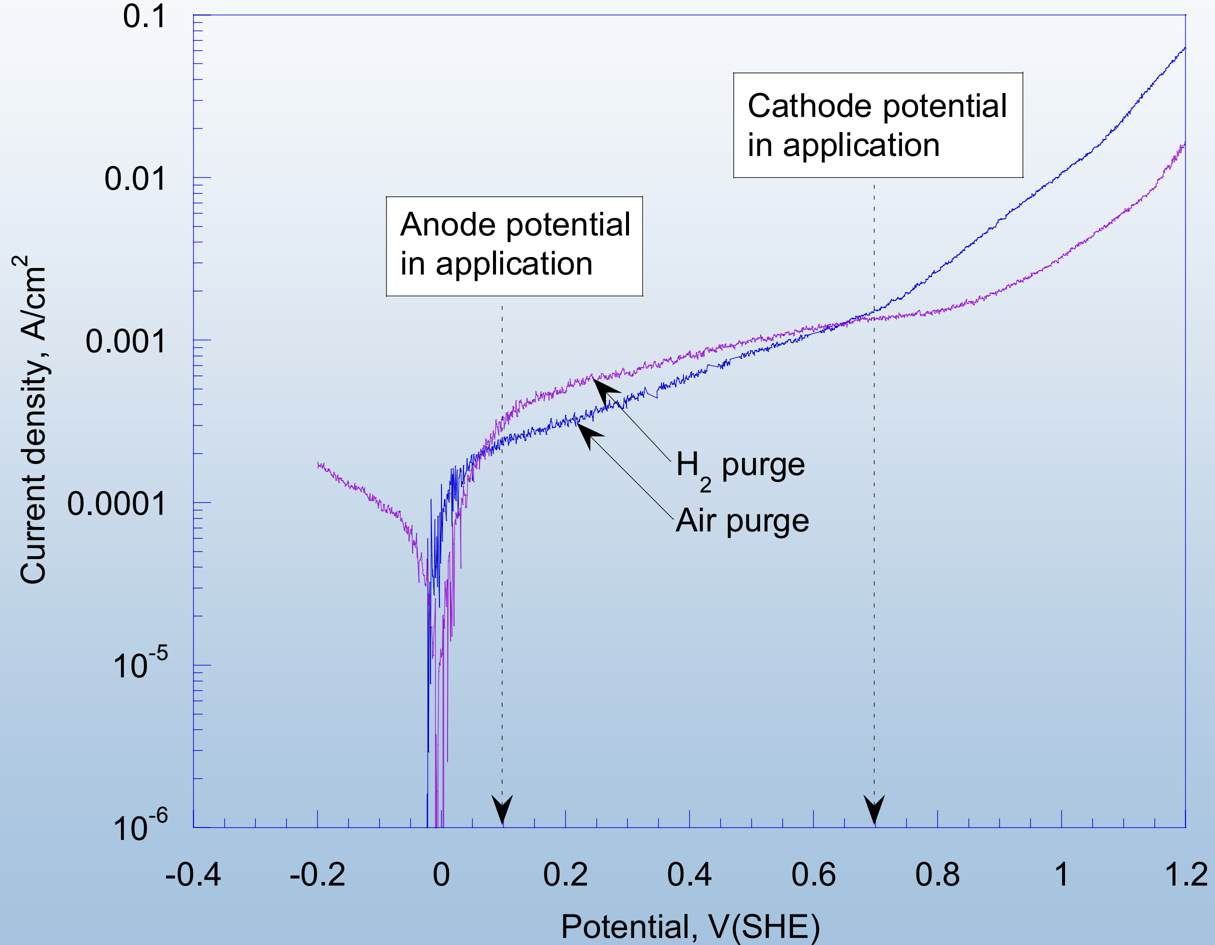

- At 0.1 V with $H_2$ purge, current slightly increases from 0.73 to 1.15 mA/cm$^2$ after 15 minutes;
- At 0.7 V with air purge, current peaks at 5 minutes, then stabilized at 1.0-1.25 mA/cm$^2$ after 15 minutes;
- Matches with dynamic polarization.

# How about graphite (used in PAFC now)?




- Actual bipolar plate;
- Very low ICR with graphite;
- Tested at room temperature

# Anodic behavior of graphite in $H_3PO_4$ at 170 °C with $H_2$ or air purge




- High currents
- 2 Tafel regions.

# Dissemination of Results

## Journal Papers

1. Heli Wang and John A. Turner:
$SnO_2$:F Coated Ferritic Stainless Steels for PEM Fuel Cell Bipolar Plates, submitted to *Journal of Power Sources*.

2. Heli Wang, Glen Teeter and John A. Turner:
Investigation of a Duplex Stainless Steel as Polymer Electrolyte Membrane Fuel Cell Bipolar Plate Material, *Journal of the Electrochemical Society*, 152 (3) B99-B104(2005).

3. Heli Wang, Michael P. Brady, Glenn Teeter and John A. Turner:
Thermally Nitrided Stainless Steels for Polymer Electrolyte Membrane Fuel Cell Bipolar Plates: Part 1: Model Ni-50Cr and Austenitic 349™ alloys, *Journal of Power Sources* 138, 86-93(2004).

4. Heli Wang, Michael P. Brady, K. L. More, H. M. Meyer III and John A. Turner:
Thermal Nitrided Stainless Steels for Polymer Electrolyte Membrane Fuel Cell Bipolar Plates, Part 2: Beneficial Modification of Passive Layer on AISI446, *Journal of Power Sources* 138, 79-85(2004).

5. Heli Wang and John A. Turner:
Ferritic Stainless Steels for Bipolar Plate for Polymer Electrolyte Membrane Fuel Cells, *Journal of Power Sources* 128, 193-200(2004).

6. Heli Wang, Mary Ann Sweikart, John A. Turner:
Stainless Steel as Bipolar Plate Material for Polymer Electrolyte Membrane Fuel Cells, *Journal of Power Sources* 115, 243-251(2003).

## Conference Papers/Presentations

1. M. P. Brady, H. Wang, I. Paulauskas, B. Yang, P. Sachenko, P. F. Tortorelli, J. A. Turner, R. A. Buchanan: Nitrided Metallic Bipolar Plates for PEM Fuel Cells, Proceedings of the 2nd International Conference of Fuel Cell Science, Engineering and Technology, Rochester NY, June 14-16, 2004.

2. Heli Wang and John A. Turner: Using Duplex, Austenite and Ferrite Stainless Steels for Bipolar Plate in PEM Fuel Cells, Proceedings of the 204th Meeting of the Electrochemical Society, October 12-16, Orlando, FL, USA, 2003, paper No. 1004.

## Paten Application

M. P. Brady, H. Wang and J. A. Turner, Surface Modified Stainless Steels for PEM Fuel Cell Bipolar Plates, US Patent Application, 2005 (pending).

# Future Work

- Continue NREL/ORNL collaboration with alloy development and nitridation
- Investigate new alloy compositions and coatings
- Bare alloys in HT PAFC environments;
- Nitrided alloys in HT environments;
- Coated steels in HT environments;
- Further NREL/PlugPower collaboration.

# Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- Hydrogen atmosphere used during corrosion tests

# Hydrogen Safety

Our approach to deal with this hazard is:

- Limit cell head space to <10ml and use low hydrogen flow rates.
- Perform experiments in a fume hood.
- Project activities are covered by a formal, standard operation procedure and reviewed by ES&H and approved by PI's and cognizant managers.